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Hybridization of Phenylthiolate- and Methylthiolate-Adatom Species at Low Coverage on the Au(111) Surface

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Supporting Information

ABSTRACT: Using scanning tunneling microscopy we observed reaction products of two chemisorbed thiolate species, methylthiolate and phenylthiolate, on the Au(111) surface. Despite the apparent stability, organometallic complexes of methyl- and phenylthiolate with the gold-adatom (RS-Au-SR, with R as the hydrocarbon group) undergo a stoichiometric exchange reaction, forming hybridized CH_3S-Au-SPh complexes. Complementary density functional theory calculations suggest that the reaction is most likely mediated by a monothiolate RS-Au complex bonded to the gold surface, which forms a trithiolate RS-Au-(SR)-Au-SR complex as a key intermediate. This work therefore reveals the novel chemical reactivity of the low-coverage "striped" phase of alkanethiols on gold and strongly points to the involvement of monoadatom thiolate intermediates in this reaction. By extension, such intermediates may be involved in the self-assembly process itself, shedding new light on this long-standing problem.

Self-assembly of thiol and disulfide molecules on the gold surface continues to be a topic of broad interest in light of the growing utility of the thiolate self-assembly in a number of research applications[1−3] as well as the need to develop a more predictive framework for tailoring molecules on surfaces. The present understanding of alkanethiolate self-assembly has been summarized in a number of review articles.[4−6] Although it is generally agreed that thiolate molecules bond to the gold surface via gold-adatoms,[7−9] the exact structural model, the number of gold adatoms bonded to the thiolate species, the degree of disorder, and the involvement of surface vacancies are still a matter of debate. But perhaps the most puzzling question is the actual mechanism of the self-assembly, and specifically the reactions by which S−H and S−S bonds dissociate, the gold adatoms are incorporated, and the subsequent self-assembly occurs. Understanding these processes is critical to allow a deterministic prediction of the experimental procedures that can lead to a well-ordered self-assembled monolayer of organosulfur molecules, the topology of the self-assembled patterns, and practical applications of the chemical reactivity of SAMs.[1]

It is widely accepted that the self-assembly of most alkanethiolates proceeds through a low-coverage, well-ordered two-dimensional phase termed the striped phase.[10] The building blocks of the striped phase are organometallic complexes produced between two thiolate species and a gold-adatom, RS-Au(ad)-RS, which is sometimes referred to as the "staple".[4,11] In the case of the shortest alkanethiolate (CH_3S), the binding energy of the CH_3S-Au-SCH_3 complex to the Au(111) surface is 167.2 kcal/mol (with respect to isolated Au and CH_3S species), which is almost twice as large as ∼86 kcal/mol of two CH_3S fragments, bonded directly to the Au(111) surface in their most stable bridge-fcc configuration.[12] Furthermore, the S−Au-adatom bond imposes strict steric constraints on the S−C bond angle relative to the surface plane, and thus upon the topology of the monolayer itself.[13] Although the evolution of the striped phase as a whole with increasing surface coverage of alkanethiolates was determined a long time ago,[14,15] so far there is a lack of experiments or calculations that have addressed the detailed mechanism by which the striped phase reacts or evolves within the Au-adatom-based picture.

Here we present a scanning tunneling microscopy (STM) study of the coassembly between methylthiolate and phenylthiolate on the Au(111) surface at low-coverage that directly confirms the ability of the RS-Au-SR complexes to undergo a substitution reaction, conceptually similar to substitution reactions of the three-dimensional phases.[14,17] The accompanying density functional theory (DFT) calculations imply the involvement of the singly coordinated adatom complexes, RS-Au, in the substitution reaction.

All the experiments were carried out in the ultrahigh vacuum environment, at a background pressure of $<5 \times 10^{-10}$ Torr as described previously.[13] Phenylthiol (PhSH) and dimethyldisulfide (CH_3SSCH_3) precursor molecules were deposited onto a clean Au(111) surface held at ∼70 K. Dissociation of the parent molecules and subsequent self-assembly of their products were carried out by slowly heating the surface to 250−300 K for up to 10 min. The surface was subsequently cooled down to 5 K for imaging in STM.

As we discussed earlier,[18] thermal dissociation of phenythiol on Au(111) at 300 K produces organometallic complexes (PhS-Au-SPh) that are stoichiometrically identical to those of

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alkanethiolates, Figure 1a. Each complex has either a cis- or trans-configuration of the phenyl groups relative to the S−Au−S bond axis. To verify the orientation of the phenyl rings in these complexes, we have optimized their adsorbed structures by density functional theory calculations. The configuration shown in Figure 1b has a binding energy of 147.2 kcal/mol. The planes of both phenyl rings are tilted by 62°−65° relative to the surface normal, while the Au−S−C angles are 108.2°−110.1° Therefore, the phenyl rings are clearly registered as two round shapes in the STM images (Figure 1a and ref 18). PhS-Au-SPh complexes do not self-assemble into the striped phase in its original definition because of the steric repulsion between the phenyl groups. However, the complexes do coalesce due to hydrogen bonding between aromatic hydrogen atoms and the sulfur headgroups.[18]

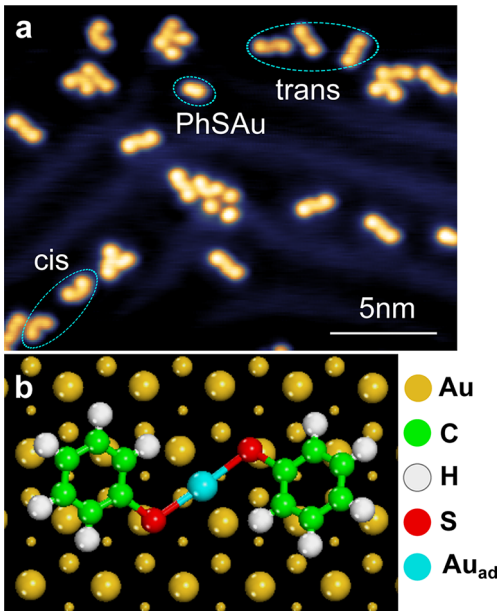

Figure 1. (a) STM image of PhS-Au-SPh complexes on the Au(111) surface. (b) Ball-model representation of the DFT-optimized structure of the trans-PhS-Au-SPh complex adsorbed on the Au(111) surface. Au_{ad} is the gold adatom.

To induce the hybridization reaction between phenyl- and methylthiolate, dimethyldisulfide was deposited onto the gold surface with a preformed low coverage of phenylthiolate complexes (as in Figure 1a) at 70 K. Subsequently, the gold crystal was heated up to 300 K and cooled back to 5 K for STM imaging. Upon careful inspection of the STM images acquired after these procedures (Figure 2), three kinds of reaction products could be identified on the gold surface: (a) ordered 1D methylthiolate/Au stripes (e.g., ms in Figure 2a); (b) intact trans and cis PhS-Au-SPh complexes (pt and pc, respectively, in Figure 2a); (c) new hybrid reaction products (e.g., th, ch, respectively, in Figure 2a), which can be readily identified as an adatom complex PhS-Au-SCH_3. The identification is based on the discernible round shape of one phenyl ring on one side of the complex (Figure 2b white circle), a central feature corresponding to the adatom in the middle, and a methyl group on the other side of the complex (Figure 2b red circle). Moreover, the long axis of the complex is oriented almost normal to the $\langle 1\bar{1}0 \rangle$ direction of the gold surface, very similar to the orientation of the 1D stripes of methylthiolate. The

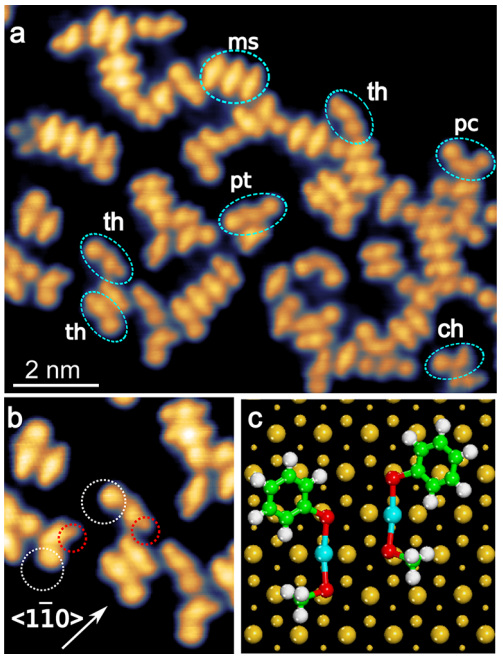

Figure 2. (a) STM image of the reaction products of the adsorption of CH_3SSCH_3 molecules onto a gold surface with a small coverage of PhS-Au-SPh complexes (Figure 1a). The labeled complexes are: ms-CH_3S-Au-SCH_3 stripe; pc(pt)-PhS-Au-SPh cis(trans) complexes; th(ch)-hybrid PhS-Au-SCH_3 trans(cis) complex formed upon the exchange reaction. (b) A close-up image of the area in (a) with several hybrid complexes. White (red) outlines mark the phenyl (methyl) groups, respectively. (c) A DFT-optimized structural model of cis-PhS-Au-SCH_3 complexes.

reaction between methyl- and phenylthiolate can therefore be represented as

$$\frac{1}{2}\text{PhS-Au-SPh} + \frac{1}{2}\text{CH}_3\text{S-Au-SCH}_3 \rightarrow \text{PhS-Au-SCH}_3 \quad (1)$$

Methyl and phenyl groups can be arranged in both cis (ch) and trans (th) relative positions around the S−Au−S bond axis in the hybrid complex (Figure 2a,b), with the majority of the complexes being trans. DFT calculations indicate a trans−cis isomerization barrier of about 11.5 kcal/mol (Supporting Figure S1), comparable to that of the methylthiolate complexes.[13,19] Although we only acquired a limited set of STM images, we can verify that the substitution reaction was the only chemical transformation of the original phenylthiolate complexes, ruling out the desorption and decomposition reactions. The density of the phenyl groups before the hybridization reaction was measured to be 0.19 and 0.24 groups/nm^2 from two separate large-scale STM images, while following the reaction the density was 0.14 and 0.23 groups/nm^2. The scatter in numbers originated from the nonuniformity of the surface coverage due to the herringbone reconstruction, where the molecular species preferentially adsorb within periodically alternating fcc-stacked regions on the surface.[7,20]

The mere fact of hybridization unambiguously confirms that contrary to the intuitive notion of the "robustness" of the RS-Au-SR complex, it turns out to be reactive around 300 K and the S−Au(adatom) bond can be broken and reformed. Unfortunately, the STM images and the location of the complexes provide few clues for the mechanism of the respective reactions. The hybridized PhS-Au-SCH_3 complexes

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can sometimes be found as isolated species, but most frequently they either pair with another CH_3S-Au-SCH_3 or decorate the end of a CH_3S-Au-SCH_3 stripe (Figure 2). This observation confirms the identity of the hybrid complex as another type of the organometallic complex. However, it does not hint as to how a hybridization reaction may occur, because aggregation with another complex could have easily happened after the hybrid had formed.

We have therefore turned to DFT calculations to identify the possible reaction pathways and evaluate the plausibility of these pathways based on the magnitude of the activation barriers involved. Our first model was the hybridization and adatom rearrangement between PhS-Au-SPh and CH_3S-Au-SCH_3 complexes, with the initial relative orientation and spacing of the two complexes chosen to resemble that in the striped phase (Supporting Figure S2). Experimentally, we do observe a number of such "dimers" (see pt in Figure 2a for example). We have explored two reaction pathways: (1) a simultaneous exchange, where the S−Au−S bonds of the two complexes break and exchange with each other at the same time; (2) a sequential exchange, similar to (1), but separated in several consecutive steps (first, forming a trimer RS-Au-(RS)-Au-SR and a lone RS, followed by the reassociation into two RS-Au-SR dimers). For the reaction to occur in the temperature range between 250 and 300 K on the time scales of a typical annealing cycle (∼10 min), the upper bound of the activation barrier height should be between 11 and 15 kcal/mol (estimated from the Arrhenius rate equation and a prefactor of 10^{13} s^{-1}).

The climbing-image nudged-elastic bands DFT calculation[21] of the simultaneous exchange scenario between a PhS-Au-SPh and CH_3S-Au-SCH_3 pair revealed a prohibitively large activation barrier of ∼33 kcal/mol (see Supporting Figure S2). A consecutive scenario lowers this barrier, but only a range of 19.4−20.1 kcal/mol depending on which molecule in the pair complex is dissociated first as seen in Supporting Figure S3. The lowest barrier calculated for the hybridization between PhS-Au-SPh and CH_3S-Au-SCH_3 complexes was 19.1 kcal/mol (see Figure S4). For reference, the reaction between two methylthiolate complexes, wherein two *trans*-CH_3S-Au-SCH_3 complexes become two *cis*-CH_3S-Au-SCH_3 complexes, has a barrier of 19.4 kcal/mol (see Figure S3). Altogether such values for the activation barrier are expected to be too large for the relevant temperature range based on the aforementioned estimate.

While it may be anticipated that the reason for the relatively high activation barriers in both cases (see Figures S3 and S4) is the large energy of the S−Au adatom bond, a closer inspection of the NEB trajectories reveals that the highest points actually correspond to the configuration where the RS-Au adatom entity (Figure S4 and Figure S5) is displaced from its 2-fold bridge site to approximately an atop site on the Au(111) surface. Thus the energy peaks when CH_3S begins to displace away from the parent complex, *after* the S−Au(ad) bond has been broken. A straightforward inspection of the lattice spacings and of the allowed adsorption sites available for the reaction leads to the conclusion that this unfavorable geometry cannot be avoided if one wants to maintain a closely spaced transition-state complex of two dissociating/hybridizing RS-Au-SR complexes.

We therefore explored an alternative route to hybridization, where CH_3S-Au (or PhS-Au) species, rather than the CH_3S-Au-SCH_3 complex, participate in the hybridization reaction (Figure 3). Reaction 1 is then split in at least two steps, for example:

$$CH_3SSCH_3(ad) + 2Au(ad) \rightarrow 2CH_3S\text{-}Au \quad (2a)$$

$$CH_3S\text{-}Au + PhS\text{-}Au\text{-}SPh \rightarrow Au\text{-}SPh + CH_3S\text{-}Au\text{-}SPh \quad (2b)$$

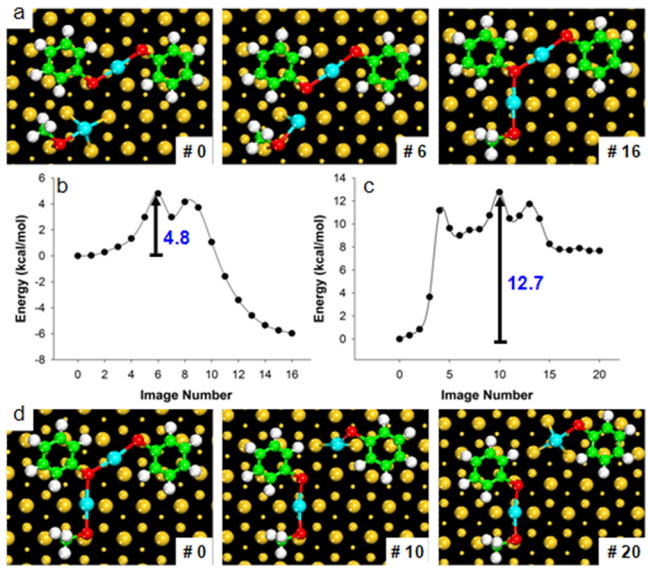

Figure 3. Minimum energy pathways for (a,b) reaction of CH_3S-Au with PhS-Au-SPh with the formation of CH_3S-Au-(SPh)-Au-SPh intermediate complex followed by (c,d) separation reaction of the PhS-Au fragment with formation of CH_3S-Au-SPh. For each reaction the atomic configurations in the initial, several transition, and final states are indicated.

The CH_3S-Au or PhS-Au species as reactants in the hybridization reaction can overcome the energetically prohibitive intermediate states, by allowing CH_3S-Au to approach the PhS-Au-SPh complex (or PhS-Au to approach the CH_3S-Au-SCH_3 complex) through a series of diffusion steps, each of which has a barrier <5 kcal/mol (with similar values for both CH_3S-Au and PhS-Au, and consistent with calculations by Cometto et al.[22]). For CH_3S-Au we considered both lying down and vertical initial configurations prior to hybridization, as shown in Figure 3 and in Supporting Information (Figure S5a). Once in a favorable position, the two reactants form an intermediate tricentric organometallic complex, CH_3S-Au-(SPh)-Au-SPh (Figure 3a), which is surprisingly stable thermodynamically. The lowest barrier calculated for this process is only ∼4.8 kcal/mol (Figure 3b), while the net energy gain is 6 kcal/mol relative to PhS-Au-SPh and CH_3S-Au bonded in their preferred configurations on the Au(111). Subsequent separation of the Au-SPh fragment now proceeds through a maximum barrier of ∼12.7 kcal/mol (Figure 3c,d), which is feasible for the temperature range of our experiments. Thus, invoking RSAu species in the hybridization reaction reduces the maximum activation barrier height by as much as ∼15 kcal/mol, relative to the simultaneous exchange mechanism between a PhS-Au-SPh and a CH_3S-Au-SCH_3 pair. In the case when a PhS-Au group reacts with a CH_3S-Au-SCH_3 molecule the corresponding diffusion and hybridization barriers are also relatively small with values less than 6.2 kcal/mol (see Figure S5b). Therefore, both scenarios for hybridization, including either reaction of CH_3S-Au with PhS-Au-SPh or reaction of PhS-Au with CH_3S-Au-SCH_3 are kinetically feasible.

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The existence of the RS-Au adatom complexes on the surface requires justification. At present the reaction pathway from an adsorbed thiol RSH or dimethyldisulfide RSSR molecule to the organometallic complexes is not fully understood.[4−6] But the mere fact that chemisorption of thiol RSH molecules yields the same type of adatom complexes as RSSR[8] suggests that the RS-Au species must form and exist on the surface at some point in the temperature range corresponding to the self-assembly reaction. Also, in the case of phenylthiolate, we do observe features that could be assigned to PhS-Au (Figure 1a). At the same time, earlier theoretical models and several experiments have implicated RS-Au species as the actual building blocks of the SAMs.[7,23,24] Cometto et al. suggested that RS-Au species may be the favorable intermediate in the self-assembly process based on the lower diffusion barrier compared to both RS and the gold adatom itself over the gold surface.[22] Moreover, a model for the $\sqrt{3}x\sqrt{3}R30°$ phase of the methylthiolate on gold at 300 K proposed by Mazzarello et al.[23] involves a dynamic equilibrium between the CH_3S-Au-SCH_3 complexes and bridge-bonded CH_3S-Au species supported by the DFT-MD calculations. From our own DFT-NEB calculations, the barrier height to break a single S-Au-S headgroup, forming a CH_3S-Au species and a bridge-fcc bonded CH_3S fragment was calculated to be ∼16.6 kcal/mol (Figure S6a). The barrier to break PhS-Au-SPh and form PhS-Au species is only 15.9 kcal/mol (Figure S6b). Both values are on the borderline of thermally allowed reactions around 300 K, and we therefore cannot exclude the possibility of a nonzero equilibrium surface coverage of CH_3S-Au or PhS-Au coexisting with, respectively, $CH_3SAuSCH_3$ and PhS-Au-SPh during the hybridization reaction. In addition, the involvement of defect sites such as atomic steps or dislocation sites on the herringbone reconstruction may play a role in reducing the activation energy for these individual bond breaking steps.

To summarize, we have directly observed a first example of hybridization reaction between alkyl- and phenylthiolate species, bonded to the surface in the form of organometallic complexes with gold adatoms. Using density functional theory, we have evaluated a series of possible reaction pathways that lead to hybridization and concluded that a direct reaction between two organometallic complexes is unlikely. However, involving singly coordinated CH_3S-Au complexes does allow for an exchange reaction with the PhS-Au-SPh complexes through a tricentric intermediate, with a maximum barrier height of ∼12.7 kcal/mol. More generally, our observations emphasize that the striped phase by itself is reactive at around 300 K, and S−Au−S bonds can be broken. The evolution toward the high coverage 3D ordered phase through a series of striped phases must consider the possibility of such ligand exchange reactions as well as the likely involvement of RS-Au intermediates in the process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supplementary DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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